



Analysis of the deactivation of Pd, Pt and Rh on activated carbon catalysts in the hydrodechlorination of the MCPA herbicide

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ABSTRACT

The deactivation of a palladium on activated carbon (Pd/AC) catalyst in the hydrodechlorination (HDC) of the organochlorinated herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) in water under ambient-like conditions has been studied. The loss of activity is attributed to the accumulation of organic species involved in the reaction on the catalyst surface. The analysis of the fresh and used catalysts indicated the possibility of regeneration by thermal or washing (water, NaOH solutions) treatments. Bimetallic catalysts, Pd-Rh/AC and Pd-Pt/AC, showed lower activity than the Pd/AC one but higher stability (slower deactivation). A Pd catalyst supported on an activated carbon modified upon oxidation (Pd/AC_{OX}) exhibited higher activity and stability which can be due to the high concentration of surface oxygen groups that reduced the uptake of fouling species.

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1. Introduction

Catalytic hydrodechlorination (HDC) represents a promising technology for the treatment of wastewater streams containing organochlorinated pollutants, which are known as persistent highly toxic compounds. HDC is a simple, safe and effective technique that can operate under mild conditions (temperature and pressure) and is suitable for the treatment of a diversity of chlorinated compounds within a wide range of concentrations. It has been demonstrated that HDC allows the conversion of those contaminants into harmless or much less toxic reaction byproducts with catalysts using precious metals as active phase. The chlorinated compounds found in wastewaters include mainly aliphatic and aromatic species. Some of them have been listed as priority pollutants by the European Commission (pentachlorophenol, dichlorobenzene, alachlor, atrazine, chlorfenvinfos, diuron, isoproturon) [1]. Currently, 4-chloro-2-methylphenoxyacetic acid (MCPA) is a main ingredient in about one-third of commercial phenoxy herbicides [2]. Supported catalysts based on Pd, Rh, Ru, or Pt, as active phase, and alumina or activated carbon (AC) as support have shown high HDC activities but frequently accompanied by rapid deactivation. That deactivation is a complex phenomenon which has been attributed to chloride poisoning, metal sintering, leaching of the active phase or surface fouling [3–8]. Different

species have been tested as potential poisons in deactivation studies. The evolution of the target compound conversion or of the reaction rate along the use of the catalyst have been followed under known concentration of those species, like toxic metals, cyanogens and strongly-adsorbing organic molecules or ions. In general, the presence of SO_4^{2-} , NO_3^- and NO_2^- , can cause a slight decrease of activity [9,10], whereas the addition of SO_3^- or HS^- provoked a complete deactivation of the catalysts [9–11], as well as the existence of iodide [11], heavy metals [11] or low concentrations of soil extracts [12] in the aqueous phase. Concerning to the presence of chloride, there is no consensus. Some authors state that Cl^- does not affect to the catalytic activity [9–11], while others have observed a negative effect [13]. The evolution of the morphological, textural and chemical properties of the fresh and used catalysts have been analyzed in a number of studies [5,6,13–22]. Yuan and Keane [5] and Keane [14] attributed the loss of activity of Pd/Al₂O₃ and Pd/AC catalysts in the HDC of chlorophenols to a combination of Pd leaching, alteration of Pd dispersion, structural breakdown of the support and HCl poisoning. The deactivation of Pd/AC catalyst was more severe. Moreover, in a detailed study on the influence of Pd particle size in deactivation concluded that particles larger than 4 nm were more resistant to the corrosive action of HCl [15]. Molina et al. [16,17] attributed the deactivation of monometallic Rh and bimetallic Pd-Rh on pillared clay catalysts in the HDC of 4-chlorophenol (4-CP) to the deposition of carbon-containing species on the catalyst surface which could partially block active centers and produce structural damage of the pillared clay. Meanwhile, Hildebrand et al. [18] studied the activity of a Pd on magnetite

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catalyst in the HDC of trichloroethylene (TCE), and found that deactivation was due to some sort of aging of the catalyst surface and stabilization of the Pd centers. Ordoñez et al. [13] and de Pedro et al. [7] studied the deactivation of Pd/Al₂O₃ and Pd/AC catalysts in the HDC of TCE and 4-CP, respectively. They explained the loss of activity by the interaction between the chloride ions and Pd through the formation of palladium chloride complexes. In both cases, Pd/AC catalysts showed higher resistance to deactivation than Pd/Al₂O₃, associated with the hydrophobic character of the activated carbon and its affinity for the chloride ions resulting from the HDC reaction, thus protecting the metallic active phase. In a recent paper, our research group found that the deactivation of a Pd/AC in the HDC of 2,4-dichlorophenol (2,4-DCP), 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) was mainly due to the accumulation of organic species on the catalyst surface, showing this catalyst a high resistance to chloride poisoning [22].

An important point to be considered regarding to catalyst deactivation is the possibility of recovering the activity upon regeneration. This requires to learn on the causes of deactivation. Oxidative thermal or washing treatments are addressed to the removal of the poisoning species from the surface of the catalyst [10,23–26]. Complete recovery of the initial activity of Pd/Al₂O₃ and Pd/AC catalysts used in the HDC of TCE has been reported upon washing with 20 mM sodium hypochlorite [23] and water [26]. When deactivation is caused by leaching of the active metal or structural breakdown of the support, regeneration is not possible.

Among the strategies to control deactivation, the synthesis of more robust catalysts appears the most rewarding. Previous studies have established that oxidative treatments of the activated carbon support with HNO₃, H₂O₂ and (NH₄)₂S₂O₈ leads to the formation of surface oxygen groups which affect to the activity and stability of the catalyst by modifying the adsorption of species involved in the reaction [27–31]. Another possible option to obtain highly active and more stable catalysts is the synthesis of bimetallic ones [16,32]. Witonska et al. [19] and Krolak et al. [21] concluded that the addition of Bi or Tl improved the stability of a Pd/Al₂O₃ and a Pd/SiO₂ catalyst, respectively. Interesting results were obtained with the Pd-Bi/Al₂O₃ catalyst, allowing complete conversion of 2,4-DCP maintained upon 7 reaction cycles whereas with Pd/Al₂O₃ only 50 % conversion was achieved. In addition, Wu et al. [33] found that a bimetallic Pd-Au/Fe₃O₄/SiO₂ catalyst showed much better stability than the monometallic Pd/Fe₃O₄/SiO₂ in the 4-CP HDC. The effect of Au was also tested in the HDC of TCE with nanoparticle (NPs) catalysts. Pd/Au NPs were more resistant to deactivation than Pd NPs [34–36].

The aim of this work is to analyze the deactivation and the possibility of regeneration of a Pd/AC catalyst used in the HDC of MCPA, a chlorinated herbicide widely used for the control of plant growth. In a previous work, it has been demonstrated that this catalyst suffered a progressive and deep deactivation along HDC upon 100 h on stream. Regeneration is also studied by several ways, including washing and oxidation-reduction cycles, which serve as well to gain evidences on the causes of deactivation. Modification of the activated carbon support by oxidation and the use of bimetallic Pd-Rh and Pd-Pt catalysts are also checked as possible improved solutions.

2. Experimental section

2.1. Catalysts preparation and characterization

A palladium catalyst (Pd/AC, 0.5% wt.) was prepared in our lab by incipient wetness impregnation of an activated carbon supplied

by Merck (BET surface area $\approx 950 \text{ m}^2/\text{g}$; pore volume $\approx 0.43 \text{ cm}^3/\text{g}$; bulk density $\approx 0.5 \text{ g/cm}^3$; particle size $\approx 1.5 \text{ mm}$). Another palladium catalyst (Pd/AC_{OX}, 0.5% wt.) was prepared using the same carbon after an oxidative treatment with HNO₃ which was carried out by boiling 1 g of the activated carbon in 10 mL of a 6 N HNO₃ solution for 20 min [37]. In both cases, the impregnating solution consisted in PdCl₂ (Sigma–Aldrich) dissolved in 0.1 N HCl aqueous solution. The volume of that solution exceeded by 30% the total pore volume of the activated carbon. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 °C. Finally, the catalysts were calcined at 200 °C for 3 h in air atmosphere and reduced at 150 °C for 1.5 h under continuous H₂ flow.

Bimetallic catalysts (Pd-Rh/AC; Pd-Pt/AC) were prepared following a similar procedure. The metal bulk content was 0.5% wt. in all cases (0.25% wt. of each metal). The impregnation solution consisted in an appropriate mixture of PdCl₂ and RhCl₃ (Sigma–Aldrich) or PdCl₂ and PtCl₂ (Sigma–Aldrich) dissolved in 0.1 N HCl aqueous solution. All the catalysts were sieved and the 1–2 mm size fraction was used in the HDC experiments.

The BET surface area, micropore volume and narrow mesopore (2–8 nm) volume were determined from the 77 K N₂ adsorption–desorption isotherms (Tristar 3020, Micromeritics). The external or non-micropore area was obtained from the *t*-method and the micropore volume from the Dubinin–Raduskevich equation. The elemental composition of the catalysts was analyzed by a CHNS analyzer (LECO CHNS-932). Thermogravimetric analyses were performed in a Mettler SDTA851e model TGA apparatus under 50 NmL min^{−1} continuous N₂ flow. A weighted amount (approaching 20 mg) of sample was heated at 2 °C min^{−1} up to 110 °C, temperature that was maintained for 1 h to remove completely the humidity. Subsequently, the samples were heated at 2 °C min^{−1} up to 550 °C and at 5 °C min^{−1} up to 800 °C. The amount of surface oxygen groups of the catalysts was determined by temperature-programmed desorption (TPD), heating the samples up to 900 °C in N₂ flow at a heating rate of 10 °C min^{−1} and analyzing the CO and CO₂ evolved by means of a non-dispersive infrared absorption analyzer (Siemens, Ultramat 22).

Inductively coupled plasma-mass spectroscopy (ICP-MS) was used to analyze the bulk Pd, Rh and Pt contents, by means of a model Elan 6000 Sciex PerkinElmer apparatus. Previously to ICP-MS analyses, the samples were digested for 15 min in a high pressure microwave oven using aqua regia at 250 °C. Surface concentrations of Pd, Rh, Pt and Cl were determined by X-ray photoelectron spectroscopy (XPS) with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer (pass energy of 20 eV) and a Mg KR ($h\nu = 1254.6 \text{ eV}$) X-ray source, powered at 120 W. The binding energies of the Pd 3d_{5/2}, Rh 3p_{3/2} and Pt 4f_{7/2} core levels and full width at half maximum (FWHM) values of the corresponding peaks were used to assess the chemical state of Pd, Rh and Pt. Since the Al 2p peak of the support overlaps with the Pt 4f doublet, the contribution of Al to Pt quantification was estimated from the Al 2s signal and subtracted. Correction for binding energies due to sample charging was effected by taking the C 1s peak (284.6 eV) as an internal standard. For the analysis of the peaks a Shirley-type background was used. The peaks were adjusted to a combination of Gaussian and Lorentzian functions using the XPSPeak 4.1 software.

The metal dispersion of the catalysts was calculated from the CO chemisorption data obtained at room temperature in a Micromeritics Chemisorb 2750 automated system equipped with ChemiSoft TPx software. Before the chemisorption tests, the samples were reduced in H₂ flow (50 NmL min^{−1}) at 150 °C for 2 h and then cooled down to ambient temperature in He flow (20 NmL min^{−1}). To calculate the metal dispersion, the stoichiometry of the CO adsorption over Pd, Pt and Rh was assumed to be 1:1 [38].

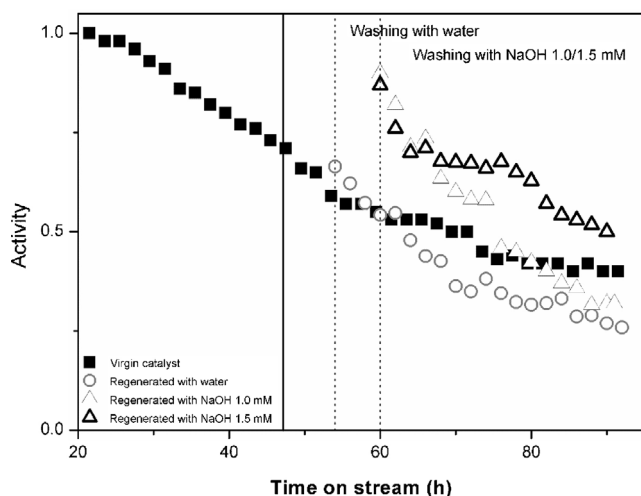


Fig. 1. Evolution of the activity of the virgin and regenerated (washing treatments) Pd/AC catalysts upon time on stream. Activity as defined by Eq. (3). Black line indicates the beginning of the experiment with the regenerated catalysts. Discontinuous lines indicate the time in which the pseudo-stationary state was again reached.

2.2. Experimental set-up and procedure for the HDC runs

Three replicates of each HDC run were carried out in a 300 mL continuous stirred basket tank reactor (Carberry Spinning Catalyst Basket) from Autoclave Engineers, provided with temperature, pressure, gas and liquid flow control. Constant gas flow rate and reactor pressure were maintained by means of a mass flow controller and a back-pressure control valve, respectively. The reactor was heated up to the reaction temperature, measured and controlled by a thermocouple in the liquid phase. Aqueous solution of MCPA (0.705 mM; 4 mL min⁻¹) and hydrogen (50 NmL min⁻¹) were continuously fed to the reactor. A catalyst concentration of 2.75 g L⁻¹ was always used, so that the space-time was fixed at 2.95 kg_{cat} h mol_{MCPA}⁻¹. All the experiments were performed at 30 °C and atmospheric pressure and the stirring velocity was maintained at 600 rpm. The progress of the reaction was followed by taking liquid samples periodically from the reactor exit with a fraction collector (FC203B-Gilson) along the time on stream of the experiments.

The data reproducibility was better than ±5%. Mass-transfer limitations can be discarded in our operating conditions as established in previous works [39,40]. Although in those works 4-CP was used as target compound instead of MCPA, it should be considered that the estimated diffusion coefficient of MCPA is quite similar to that of 4-CP (7.67 × 10⁻¹⁰ vs. 9.39 × 10⁻¹⁰ m²/s) [41] and the reaction rate is slower in the case of MCPA.

The Pd/AC catalyst was regenerated after 48 h on stream under the aforementioned reaction conditions. Two of the regeneration processes tested were based on thermal treatments. The first consisted on drying at 120 °C for 1 h and heating at 200 °C in air atmosphere for 3 h, while the second included the same drying and heating steps followed by reduction under continuous H₂ flow at 150 °C for 2 h. Two washing procedures were also checked for regeneration, using distilled water and NaOH solution (1.0–1.5 mM) for 8 h under the following conditions: 30 °C, 1 atm, 600 rpm, 50 NmL min⁻¹ of N₂. The washing liquid flow was always 5 mL min⁻¹. When using NaOH solutions, the catalyst was then rinsed with distilled water. Once the regeneration process was finished, the catalysts were tested again in the HDC of MCPA under the already described conditions for 48 h.

Adsorption tests were carried out in stoppered glass bottles (100 mL) placed in an orbital shaker (Julabo shake Temp, model SW-22) at 200 rpm equivalent stirring velocity and 30 °C. MCPA

aqueous solutions were prepared with concentrations from 0.08 to 1.5 mM. A volume of 50 mL was placed in contact with 25 mg of activated carbon (AC or ACOX) or catalyst (Pd/AC or Pd/AC_{OX}) for more than 24 h. The equilibrium data were fitted to the Langmuir equation [42].

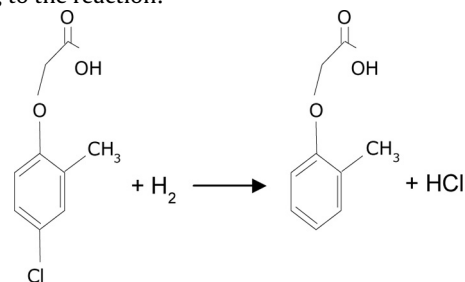
2.3. Analytical methods

MCPA and 2-methylphenoxyacetic acid (MPA) were quantified by HPLC (Varian Prostar 325) with a UV detector at 280 nm using a C18 column as stationary phase (Valco Microsorb-MW 100-5C18; 150 × 4.6 mm) and a mixture of acetonitrile and 0.1% aqueous acetic acid as mobile phase at 0.5 mL min⁻¹. Chloride was analyzed by ionic chromatography (Metrohm 790 Personal IC) using a Metrosep A Supp 5 column and 0.7 mL min⁻¹ of a buffer NaHCO₃ (1 mM)/Na₂CO₃ (3.2 mM) solution as mobile phase. The pH was measured with a pH meter (CRISON). Analyses of Pd, Pt and Rh in the liquid stream exiting the reactor were carried out by total reflection X-ray fluorescence (TXRF) with a TXRF EXTRA II spectrometer.

3. Results and discussion

3.1. HDC of MCPA with Pd/AC

The HDC of MCPA with Pd/AC led to MPA in addition to HCl according to the reaction:



MPA, the reaction product from MCPA HDC yields significantly higher EC₅₀ value (150–300 mg L⁻¹) [22,43] than the starting MCPA (12–75 mg L⁻¹) [22,43–46], thus HDC allows an important reduction of ecotoxicity.

The pH of the reaction remained around 3–3.5. In the early stages the adsorption of reaction species onto the activated carbon hinders to close the carbon and chloride balances. However, once the steady state was reached (≈20 h) the carbon and chloride balances were always matched above 95 and 97 %, respectively.

The evolution of the activity of the Pd/AC catalyst upon time on stream is depicted in Fig. 1. The activity has been calculated as the rate of MCPA disappearance at a given time on stream relative to the initial one, corresponding to the start of the pseudo-steady state. A progressive deactivation of the Pd/AC catalyst is evident, which has been attributed to the adsorption of organic species involved in the reaction [22]. From that deactivation hypothesis, an efficient regeneration would be possible by releasing the adsorbed species from the catalysts surface. Thermal regeneration by the oxidative and the oxidative plus reduction treatments described before did not allow any significant recovery of the catalytic activity. A more aggressive thermal treatment was discarded in order to avoid any modification of the structural characteristics with respect to the fresh catalyst. A different scenario was observed for the washing regeneration treatments with water or with NaOH aqueous solutions. Fig. 1 includes the evolution of the activity of the regenerated catalysts upon time on stream. In spite that the washing with distilled water did not allow any significant recovery of the catalytic activity, the HPLC analyses of the liquid from washing yielded 66 and 28 mg of MCPA and MPA per gram of catalyst, respectively, as the amounts des-

orbed after 8 h of that washing treatment. The efficiency of water washing to regenerate a Pd/AC catalyst used in the HDC of TCE was tested by Ordoñez et al. [13]. Using distilled water at 25 °C for 15 h was enough to remove the chloride ions from the catalyst, allowing complete recovery of the activity. However, this treatment was not useful in our case. The pK_a of MCPA and MPA are very close to 3. Thus, the undissociated and anionic species would exist in the reaction medium, which was within the pH range of 3.0–3.5. At this pH, the surface of the catalysts should be positively charged since their pH slurry was always around 6. Therefore, the adsorption of MCPA and MPA is governed by both hydrophobic and electrostatic interactions. Increasing the pH increases the relative abundance of the anionic species while the charge of the catalyst surface is neutralized and even reversed, thus giving rise to a lower adsorption [47]. Thus, some more severe washing treatments were checked by means of NaOH solutions (1.0–1.5 mM). In both cases, the initial catalytic activity was only partially recovered. The amounts of MCPA in the washing effluents were 166 and 210 mg g⁻¹ with 1.0 mM and 1.5 mM NaOH, respectively, while the MPA amounts were around 50 mg g⁻¹ in the two runs. In all the cases, the activity of the regenerated catalyst fell rapidly upon time on stream. This is consistent with deactivation being caused by fouling of the catalyst surface by adsorption of species involved in the reaction. Similar values of the residual activity were observed for the original Pd/AC catalyst and the NaOH-regenerated one.

The characterization of the regenerated Pd/AC catalyst under the most effective treatment (washing with a 1.5 mM NaOH solution) revealed some significant differences with respect to the used non regenerated catalyst [22]. The former showed higher BET surface (334 vs 93 m²/g), C content (85 vs 82%) and surface Pd content measured by XPS (1.56 vs 0.98% wt.), whereas its surface Cl was lower (2.2 vs 4.1% wt.). However, those characteristics of the regenerated catalyst were still far from the measured for the fresh catalyst (Table 1). These results support the accumulation of organic (in particular, organochlorinated) species on the catalyst surface as the main cause of deactivation and confirm that the NaOH washing allows only partial regeneration of the catalyst. The TGA and DTG profiles of the virgin, used and regenerated Pd/AC catalysts in N₂ atmosphere are depicted in Fig. 2. As can be seen, there are two defined peaks in the profiles of the used and regenerated catalysts, which can be associated to the MCPA and MPA, respectively. The used catalyst showed significantly higher weight-loss (up to 25%) than the regenerated one (11%), while the fresh catalyst lost only about 3.5% of its initial weight. Most of the weight-loss of the used catalyst occurred beyond the temperature of the thermal treatment applied (200 °C) consistently with the negligible regeneration observed upon that treatment.

3.2. Bimetallic Pd-Rh/AC and Pd-Pt/AC catalysts

Bimetallic catalysts were prepared and tested in the HDC of MCPA focusing on their stability. So far it is well known the HDC ability of Pd, while Rh is highly active for further hydrogenation [30,32,33]. Regarding to Pt, although it has shown less activity than Pd and Rh for HDC in aqueous phase [39,48,49], it has exhibited a superior stability in the gas phase HDC of chloromethanes [50,51].

The performance of the bimetallic Pd-Rh and Pd-Pt/AC catalysts upon 100 h on stream can be seen in Fig. 3 compared with the monometallic ones. The initial MCPA conversion was 43 and 22% with Pd-Rh/AC and Pd-Pt/AC, respectively, both significantly lower than the achieved with the monometallic Pd/AC catalyst. This must be due to the lower load of this metal (the most active) in the bimetallic catalysts (0.25 vs 0.5%). As with the monometallic Pd catalyst, deactivation is evidenced by the decrease of MCPA conversion upon the 100 h on stream of the experiments.

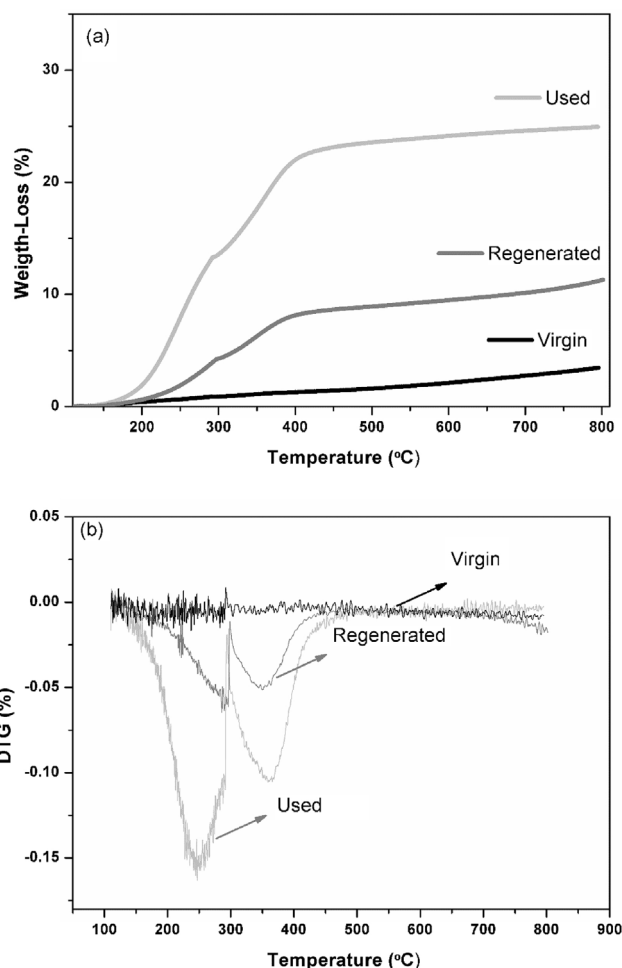


Fig. 2. TGA (a) and DTG (b) profiles of the virgin, used and regenerated Pd/AC catalyst in N₂ atmosphere.

Table 1 summarizes the characterization of the fresh and used catalysts. The BET surface area and micropore volume of the used catalysts significantly decreased with respect to those of the corresponding fresh ones and the external or non-microporous area was reduced to about one-half. The results of CO chemisorption indicated that the metallic phases were fairly well dispersed in the fresh Pd-Rh/AC catalyst and poorly in the Pd-Pt/AC one. As in the

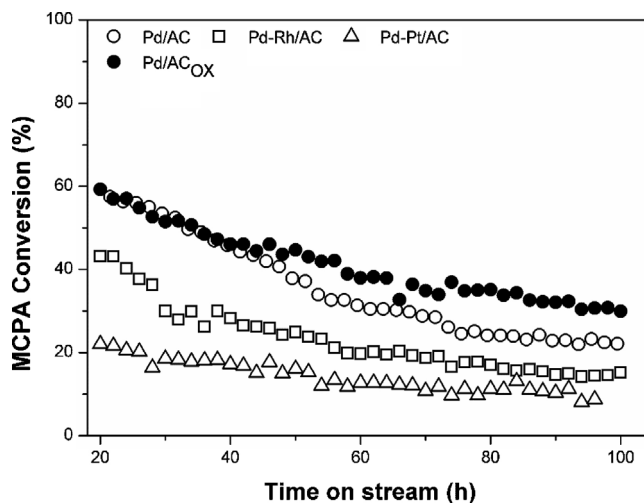


Fig. 3. Conversion of MCPA upon time on stream with the catalysts tested.

Table 1

Characterization of the fresh and used catalysts.

Catalyst	Pd/AC [22]		Pd-Rh/AC		Pd-Pt/AC		Pd/AC _{OX}	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
A _{BET} (m ² /g)	1025	93	860	70	1084	244	1004	184
A _{ext} (m ² /g)	175	81	137	65	149	78	180	100
V _{micropores} (cm ³ /g)	0.35	<0.01	0.314	<0.01	0.350	<0.01	0.350	0.031
V _{mesopores} (cm ³ /g)	0.040	0.024	0.036	0.020	0.0040	0.026	0.050	0.023
C (%)	88	82	88	81	90	82	83	88
H (%)	0.58	1.6	0.47	1.51	0.38	1.56	0.97	0.47
N (%)	0.53	0.48	0.56	0.40	0.48	0.42	0.70	0.56
S (%)	0.73	0.47	0.69	0.48	0.67	0.52	0.47	0.69
D (%) ^a	32	8	33	9	6	<1	38	25
Pd _{XPS} (% wt.)	2.55	0.98	1.42	0.65	1.27	0.93	0.86	1.65
Rh _{XPS} (% wt.)	–	–	0.73	0.40	–	–	–	–
Pt _{XPS} (% wt.)	–	–	–	–	0.38	0.15	–	–
Cl _{XPS} (% wt.)	1.9	4.1	1.56	4.47	0.29	5.29	0.66	2.42

Fresh: virgin catalyst. Used: catalyst after long-term HDC run.

^a D (%): metal dispersion.

case of Pd/AC [22], a significant decrease of the metal availability was observed in both bimetallic catalysts after their use in the HDC experiments. The ICP-MS analyses confirmed that the percentages of active metals of the fresh catalysts were in good agreement with their nominal load. TXRF measurements in the effluent from the reactor indicated negligible metal leaching in all the cases. Consequently, the apparent decrease of metal content as determined by XPS in the used catalyst can be attributed to the fouling of the catalyst surface accompanied by the corresponding mass increase rather than metal leaching. Moreover, the results from XPS show significantly higher Pd percentages than the bulk ones, suggesting that this metal is mainly distributed in the outermost surface. The XPS also showed the existence of two different metallic species, zero-valent (M⁰) and electrodeficient (Mⁿ⁺) with a higher proportion of the former in all the cases. No significant changes were found in the relative proportion of those species in all the catalysts upon their use in the HDC experiments. A remarkable increase of the amount of organic chloride was observed in all the cases in the used catalysts, consistent with the adsorption of organochlorinated species assessed as a main cause of deactivation. The TGA addressed to similar conclusions that the obtained for the monometallic Pd/AC catalyst. The weight-loss of the used catalysts was mainly detected within the range of 180–400 °C, due to desorption of the adsorbed species. In summary, all these results support the uptake of reaction species on the surface of the catalysts, causing deactivation.

3.3. Modification of the activated carbon support

A 0.5% Pd catalyst was prepared using as support the activated carbon modified upon oxidative treatment with HNO₃ as described in Section 2.1. This treatment provoked the creation of surface oxygen groups so that their amount, 2955 μmol (CO + CO₂)/g, was about 5 times that of the virgin activated carbon. However, the treatment scarcely affected to the textural properties of the final catalyst (Pd/AC_{OX}) and only small differences on the elemental composition and Pd dispersion were found (see Table 1). The Pd concentration on the external surface of the Pd/AC_{OX} catalyst, as determined by XPS, was much closer to the bulk Pd content than in the case of Pd/AC, indicative of a more homogeneous distribution of Pd onto the activated carbon particles. It presented also a somewhat higher metal dispersion (38 vs 32%). These facts are in agreement with some studies in the literature, concluding that a higher concentration of oxygen groups leads to a more hydrophilic surface which favours the interaction between the metal precursor and the activated carbon used as support [28,52].

Fig. 4 shows the 30 °C adsorption isotherms of MCPA onto the virgin and oxidized activated carbon as well as onto the correspond-

ing Pd catalysts. It can be seen that the creation of oxygenated groups on the AC surface reduced significantly the adsorption of MCPA (1.42 vs 0.95 mmol g⁻¹) in agreement with the more hydrophilic character of the AC_{OX} surface. The same trend can be observed for the catalysts, which showed somewhat higher adsorption than their corresponding supports (1.68 and 1.02 mmol g⁻¹ Langmuir capacity for Pd/AC and Pd/AC_{OX}, respectively). Trujillo-Reyes et al. [53] reported a similar effect of Pd increasing the adsorption of MCPA onto activated carbon.

These results suggest that the higher surface oxygen groups content of Pd/AC_{OX} should reduce the deactivation effect associated to the adsorption phenomenon. This can be seen in Figure 3, where a somewhat slower deactivation of the Pd/AC_{OX} catalyst is observed. From the characterization of the used Pd/AC and Pd/AC_{OX} catalysts (Table 1), it can be seen that the latter suffered a significantly lower decrease of the BET surface area, consistent with the lower blockage of the microporosity.

3.4. Kinetics of deactivation

The change of activity upon time was described by a well-known equation which includes the residual activity of the catalysts (a_∞):

$$-\frac{da}{dt} = k_d \times (a - a_{\infty}) \quad (1)$$

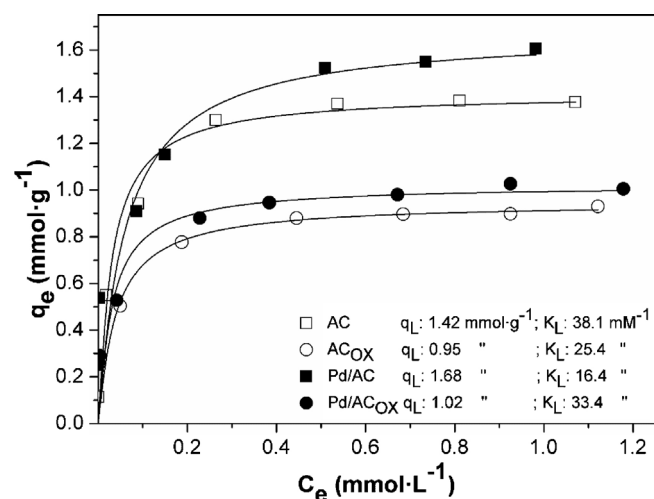


Fig. 4. Experimental data (dots) and Langmuir fits (lines) for the adsorption equilibria of MCPA onto AC, AC_{OX}, Pd/AC and Pd/AC_{OX} at 30 °C.

Table 2

Values of the deactivation constant and residual activity of the catalysts tested.

Catalyst	$(-r_{\text{MCPA}})_0$ (mmol kg _{cat} ⁻¹ h ⁻¹)	k_d (h ⁻¹)	a_∞	$\Sigma \chi^2$
Pd/AC	195	0.017 ± 0.002	0.114 ± 0.054	0.001
Pd/AC regenerated with water	129	0.053 ± 0.006	0.207 ± 0.024	0.001
Pd/AC regenerated with NaOH 1.0 mM	175	0.050 ± 0.006	0.154 ± 0.050	0.001
Pd/AC regenerated with NaOH 1.5 mM	169	0.066 ± 0.021	0.480 ± 0.061	0.002
Pd-Rh/AC	146	0.035 ± 0.002	0.300 ± 0.013	0.001
Pd-Pt/AC	75	0.022 ± 0.003	0.304 ± 0.059	0.002
Pd/AC _{OX}	201	0.021 ± 0.001	0.402 ± 0.020	0.001

where k_d is the deactivation constant (h⁻¹) and a is the catalyst activity, defined as the ratio between the reaction rate at time t and the initial. The reaction rate refers to MCPA disappearance.

From the mass balance in a continuous stirred tank reactor:

$$a = \frac{(-r_{\text{MCPA}})_t}{(-r_{\text{MCPA}})_0} = \frac{X_t}{X_0} \quad (2)$$

where X_0 and X_t correspond to MCPA conversion at the initial and t time respectively. Eq. (1) can be integrated with the limit conditions $t=0$: $a=a_0$; $t=t$: $a=a$; (being a_0 equal to 1 for the virgin catalysts). The starting time ($t=0$) corresponds to the moment when the pseudo-steady state in the effluent was reached. The resulting expression is given by:

$$a = \frac{X_t}{X_0} = (e^{-k_d \times t}) \times (a_0 - a_\infty) + a_\infty \quad (3)$$

Fitting of the experimental data to Eq. (3) was accomplished by non-linear regression (Origin 6.1). The values of the deactivation kinetic constant and the residual activity obtained in each case are given in Table 2, together with the data previously published for the Pd/AC catalyst [22] and the values of initial reaction rate. The regenerated Pd/AC catalysts yielded an initial reaction rate somewhat slower than the original catalyst and the highest values of the deactivation constant. The catalyst regenerated by NaOH washing (1.5 mM) shows the highest value of residual activity, consistent with the stability shown by this catalyst after more than 70 h on stream. As can be seen, Pd/AC and Pd/AC_{OX} catalysts yielded quite similar initial rates, slightly higher for the second, consistently with its somewhat higher Pd dispersion, whereas the achieved with the bimetallic catalysts were 30 (Pd-Rh) and 60% (Pd-Pt) lower. The Pd-Rh/AC catalyst gave a value of the deactivation constant double than that of Pd/AC. The Pd/AC_{OX} catalyst yielded a somewhat higher value of k_d than Pd/AC but a significantly higher residual activity. This last is also higher for the bimetallic catalysts compared to Pd/AC. The positive effect of using bimetallic catalysts on the stability without advantages in terms of initial activity has been described in previous works on aqueous-phase HDC [16,21,32,49,54]. Although none of the catalysts tested showed a really satisfactory stability, the modification of the activated carbon support by introducing surface oxygen groups upon oxidation appears the best solution in this case to reduce the deactivation effect caused by the adsorption of reaction species.

4. Conclusions

The Pd/AC catalyst tested in the HDC of MCPA suffered a significant and progressive deactivation up to a fairly low residual activity. Regeneration by NaOH washing allows recovering the initial activity although not completely and a fairly rapid deactivation follows again. The loss of activity seems to be caused mainly by the accumulation of organic species (especially organochlorinated) on the catalyst surface.

The bimetallic Pd-Rh/AC and Pd-Pt/AC catalysts showed somewhat higher stability than Pd/AC, without advantages in terms of

activity. The deactivation suffered by those catalysts seems to follow the same pattern than that of Pd/AC.

Modifying the activated carbon support by HNO₃-oxidation allowed improving the stability of the Pd catalyst although a similarly rapid deactivation was observed but with a significantly higher value of the residual activity. The much higher concentration of surface oxygen groups in the Pd/AC_{OX} catalyst improved the metal dispersion and reduced the adsorption of MCPA, a main cause of deactivation.

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